Effects of humic acids on the aggregation and sorption of nano-TiO$_2$

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HIGHLIGHTS

- Aromatic-rich HAs stabilized the nano-TiO$_2$ particles better than aliphatic-rich HA.
- Phenolic groups of HAs generated higher charge density on the nano-TiO$_2$ surfaces.
- Aromatic-rich HA-TiO$_2$ complexes had higher sorption and nonlinearity.

ARTICLE INFO

ABSTRACT

In this study, humic acids (HAs) from three sources, peat, sediment and straw, used to coat nano-TiO$_2$ were investigated. The results indicated that HAs isolated from peat were aromatic-rich, whereas those isolated from sediment and straw were aliphatic-rich. The nano-TiO$_2$ sedimentation experiments indicated that the presence of aromatic-rich HAs was more capable of stabilizing nano-TiO$_2$ particles than was the presence of aliphatic-rich HAs. This result is because the deionized phenolic groups in the HAs were preferentially adsorbed on the nano-TiO$_2$ surfaces, which generated a higher charge density on the nano-TiO$_2$ surfaces and caused stronger repulsive forces among particles. Furthermore, the aromatic-rich TiO$_2$-HA complexes exhibited a greater sorption capacity than the aliphatic-rich TiO$_2$-HAs complexes and nonlinear phenanthrene sorption because of their higher affinity and the condensed state of aromatic fractions. Note that natural organic matters, such as humic acids, in aquatic environments can not only increase the stability of nanoparticles but can also influence the mobility of hydrophobic organic compounds (HOCs).

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1. Introduction

Nanoparticles (NPs) are widely used in industry and in daily life because of their unique electronic, optical, thermodynamic and catalytic properties (Cohen, 2001). Because of the large number of NPs that are produced and consumed, NPs are also released into the environment and might potentially enter the food chain or drinking water sources. Furthermore, NPs might accumulate in organisms, which may consequently cause undesirable environmental and health risks (Limbach et al., 2005; Baun et al., 2008; Liu et al., 2009). The environmental transportation and transformation, as well as the organism toxicity, of NPs in aquatic environments might be strongly dependent on their sizes, surface

properties and interactions with other substances in water (Battin et al., 2009; Hofmann and Von der Kammer, 2009).

When NPs are released into aquatic environments, they interact with natural organic matters (NOM), such as humic acids (HAs), which are abundant in the environment. Previous studies have reported that NOM can significantly increase the stability of NPs in aquatic environments (Chen and Elimelech, 2007; Hyung et al., 2007; Zhang et al., 2009; Keller et al., 2010). The NOM adsorbed on the surfaces of NPs can help to maintain smaller particles sizes and more negative surface charges on the NPs (Zhang et al., 2009). Furthermore, the electrostatic double layer (EDL) repulsive energy of particles and the high energy barrier among these particles might destroy the previous balance between the attractive and repulsive potential of particles (Keller et al., 2010). Additionally, note that NPs can be stabilized by HAs through complexation between the acidic functional groups (mainly carboxylic acid) in HAs and the surface of NPs (Hajdú et al., 2009).

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On the other hand, NOM can also influence the transportation of hydrophobic organic contaminants (HOCs) through sorption processes on minerals, soils and sediments (Kang and Xing, 2005; Liang et al., 2006). It was reported that oxides coated with NOM exhibited significant sorption abilities, suggesting that NOM possessed an important role in the sorption of HOCs (Wang et al., 2008; Yang and Xing, 2009). Previous studies suggested that the sorption of HOCs on minerals coated with NOM might be related to the solution chemistry and properties of the minerals and HAs (Perminova et al., 1999; Kang and Xing, 2005). The orientations and structures of adsorbed HAs might affect the surface area of the organic phase and the accessibility of hydrophobic domains that control the sorption of HOCs (Murphy et al., 1990). The adsorbed HAs can also increase the sorption affinity and isotherm nonlinearity of phenanthrene on the surfaces of nano-TiO$_2$ and nano-ZnO by increasing the π-polarity/polarizability of adsorbed HAs (Yang and Xing, 2009). It is known that HAs in aquatic environments contain heterogeneous chemical compositions and functional groups because of the various sources from which they are obtained (Gonzalez-Vila et al., 1992; Filella, 2009) and that they might exert different influences on the stabilities and sorption abilities of NPs.

HAs are an important fraction of NOM; they are macromolecules composed of multifunctional aromatic components linked by a variety of aliphatic and acidic (mainly carboxylic and phenolic) functional groups (Hayes et al., 1989; Tombácz, 1999). In the present study, HAs extracted from three different sources were employed as the target NOM. Nano-titanium dioxide (nano-TiO$_2$) was selected as the target NPs. Nano-TiO$_2$ is an important inorganic nano-material that is widely used in many commercial applications, such as cosmetics, photocatalysts and pigments (Macwan et al., 2011). The effects of HAs on the stabilities and sorption abilities of nano-TiO$_2$ were investigated using sedimentation and sorption experiments to elucidate the relationships between the properties of HAs with heterogeneous functional groups and the aggregation and sorption behaviors of nano-TiO$_2$.

2. Materials and methods

2.1. Materials

Nano-TiO$_2$ (anatase) was purchased from the Aladdin Reagent Company, Shanghai, China. The purity, diameter and specific surface area of the nano-TiO$_2$ were >99.8%, 40 nm and 97.46 m^2/g, respectively. Three HAs were obtained from different sources (peat (HA1), river sediment (HA2), and straw (HA3)). HA1 and HA2 were extracted from peat and Pearl river sediment, respectively, according to the method recommended by The International Association of Humic Acid (Swift et al., 1996). HA3 was extracted from aqueous suspensions of rice straw that had been soaked for several weeks (Thurman and Malcolm, 1981). Phenanthrene was purchased from the Sigma–Aldrich (Shanghai) Trading Co., Ltd. All of the other solutions were prepared using analytical grade chemicals (National Medicine Corporation Ltd., Shanghai, China).

2.2. Preparation of TiO$_2$-HAs

The TiO$_2$-HA complexes were synthesized according to a previous study (Yang and Xing, 2009). Briefly, 5 g of nano-TiO$_2$ was added to 1 L of a 1 g/L HA solution in a bottle and shaken at 150 rpm for 2 d; then, the suspension was centrifuged at 4000 rpm for 30 min. The precipitated materials were then rinsed three times with Milli-Q water, freeze-dried, ground and stored for use.

2.3. Characterization of HAs and TiO$_2$-HAs

The HAs were characterized using Fourier transform infrared spectroscopy (Vector 33, Bruker, Germany), and solid-state ^{13}C nuclear magnetic resonance spectroscopy (Avance AV 400, Bruker, Switzerland) was employed to investigate the functional groups.

2.4. Effects of HAs on the Aggregation of Nano-TiO$_2$

Stock solutions of HAs (1 g/L) were prepared by dissolving the HAs in a small amount of 0.1 M KOH followed by adjusting the pH to 7 with 0.1 M HCl. To prepare the nano-TiO$_2$ dispersions in the HA solutions, HA solutions were prepared for the aggregation experiments with concentrations of 5 mg/L using stock solutions, and then the ionic strength was adjusted to 0.01 M with KNO$_3$; finally, a specific mass of nano-TiO$_2$ was added to the HA solutions. The three HA solutions were prepared under identical conditions.

Sedimentation experiments were conducted using a UV spectrometer (Shimadzu UV-2550) to monitor the dynamics of the aggregation process. Briefly, after ultrasonication for 15 min, a suspension of nano-TiO$_2$ in HA solution or a blank solution (0.01 M KNO$_3$) was placed in a cuvette and measured at 508 nm.

There was close relationship between the stability of the nano-TiO$_2$ suspension and its electrokinetic properties. In electrolyte solutions, NPs can obtain a high surface charge density, which generates strong repulsive forces. Therefore, it was important to observe the electrophoretic behavior through measurements of the zeta potential to understand the dispersion behavior of NPs in aqueous solution (Li et al., 2007). To investigate the influence of HAs on the zeta potential of the nano-TiO$_2$ aggregates, the suspensions were measured in different HA solutions and in a blank solution using a Malvern Zetasizer Nano-ZS after ultrasonication for 15 min.

2.5. Sorption experiments

The sorption experiments were conducted using a batch equilibrium technique at 25 °C and pH 7.0. Phenanthrene was mixed at a high concentration in methanol before being added to the background solution. The concentration of methanol was maintained at less than 0.1% of the total solution volume to avoid the cosolvent effect. The background solution contained 0.003 M NaN$_3$ to minimize bioactivity and 0.01 M KNO$_3$ to adjust the ionic strength. Ten to fifty milligrams of the TiO$_2$-HA complex with 15 mL of phenanthrene solution was added to a 20 mL screw cap vial equipped with a Teflon gasket and mixed for 7 d on a shaker at 150 rpm. Our preliminary experiment indicated that sorption equilibrium was reached within 7 d. After the sorption experiments, the 20 mL screw cap vial was centrifuged at 4000 rpm for 30 min, and 1 mL of the supernatant was transferred to a pre-weighed 1.5 mL amber glass vial for chemical analyses. Each concentration level, including blanks, was measured in three replicates.

The aqueous concentrations of phenanthrene were determined with reverse-phase high-performance liquid chromatography (Agilent 1200) with C$_{18}$ column (5 μm, 250 × 4.6 mm; Agilent) using a fluorescence detector with an excitation wavelength of 254 nm and an emission wavelength of 385 nm. The mobile phase (flow rate of 1.0 mL/min) was a mixture of Milli-Q water and acetonitrile in a 10:90 ratio by volume. The solid phase concentration was calculated based on the mass balance of the solute between the two phases.

The classical Henry (Eq. (1)) and Freundlich (Eq. (2)) sorption equations were used to fit the equilibrium sorption data:

$$q_e = k_d \times C_e \tag{1}$$